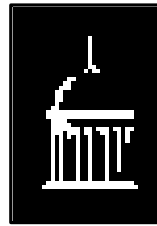


# **Effect of Ethanol on BTEX Natural Attenuation:**

Biodegradation Kinetics, Geochemistry,  
and Microbial Community Implications

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**Workshop on Ethanol & Alkylates in Fuels**  
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# Acknowledgments

## Students

- † Craig Hunt
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- † Jose Fernandez
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## Faculty/Scientists

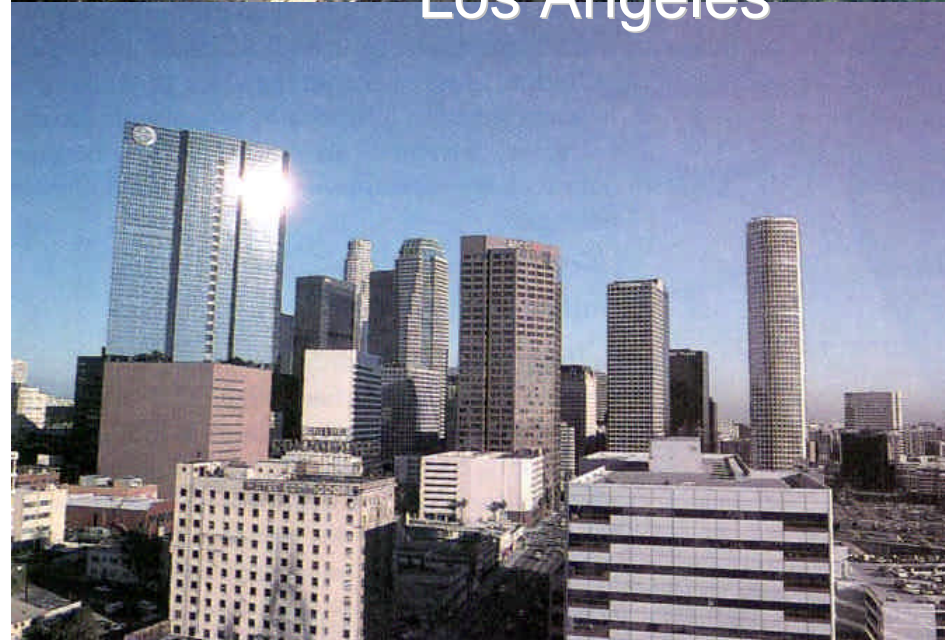
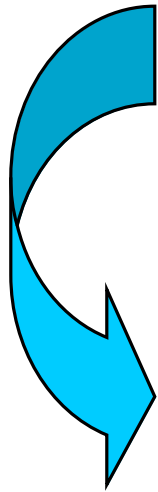
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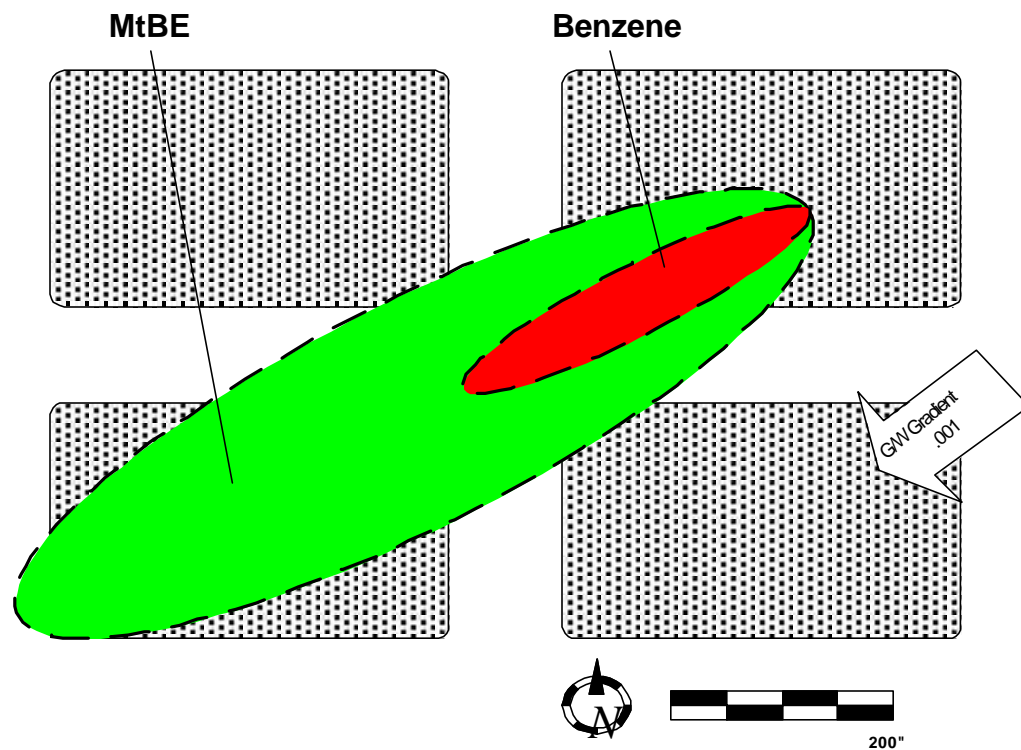
- † California/LLNL
- † EPA
- † API

Emission control regulations and gasoline reformulation reduced air pollution

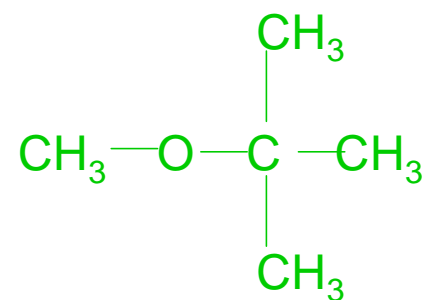
~15 years



# Distribution of Key Constituents in Gasoline-Contaminated Groundwater



MTBE



## Replace MTBE with Ethanol?

- † Good oxygenate (reduces air pollution from combustion) renewable, biodegradable, non-toxic, and can serve as substitute fuel for imported oil. But...
- † Can have adverse effects on migration and natural attenuation of priority pollutants such as benzene:
  - † Increased hydrocarbon solubility in water (cosolvent effect) and enhanced transport
  - † Inhibition of benzene biodegradation (preferential utilization, O<sub>2</sub> depletion, toxicity to bacteria if >4%)

# Prospectus

- † Do “typical” ethanol concentrations enhance BTEX migration by decreasing sorption-related retardation?
- † How does ethanol affect BTEX biodegradation rates under different electron-acceptor conditions, and how do such effects differ from one site to another?
- † Overall effect on BTEX natural attenuation and the resulting plume length?

# Methods

Breakthrough studies  
(Retardation)



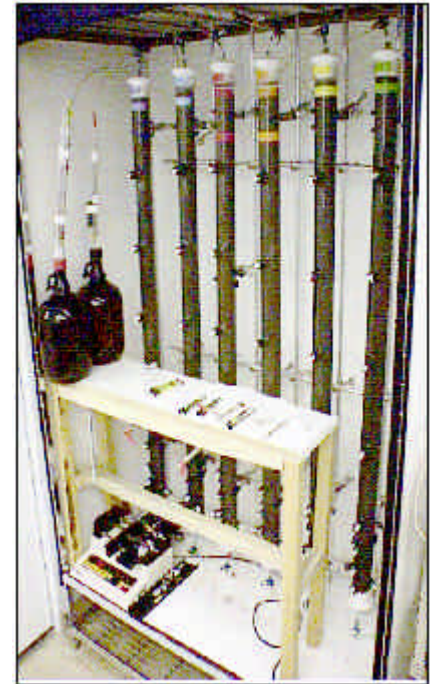
Chemostats  
(Biodegradation)



Microcosms  
(Variability)

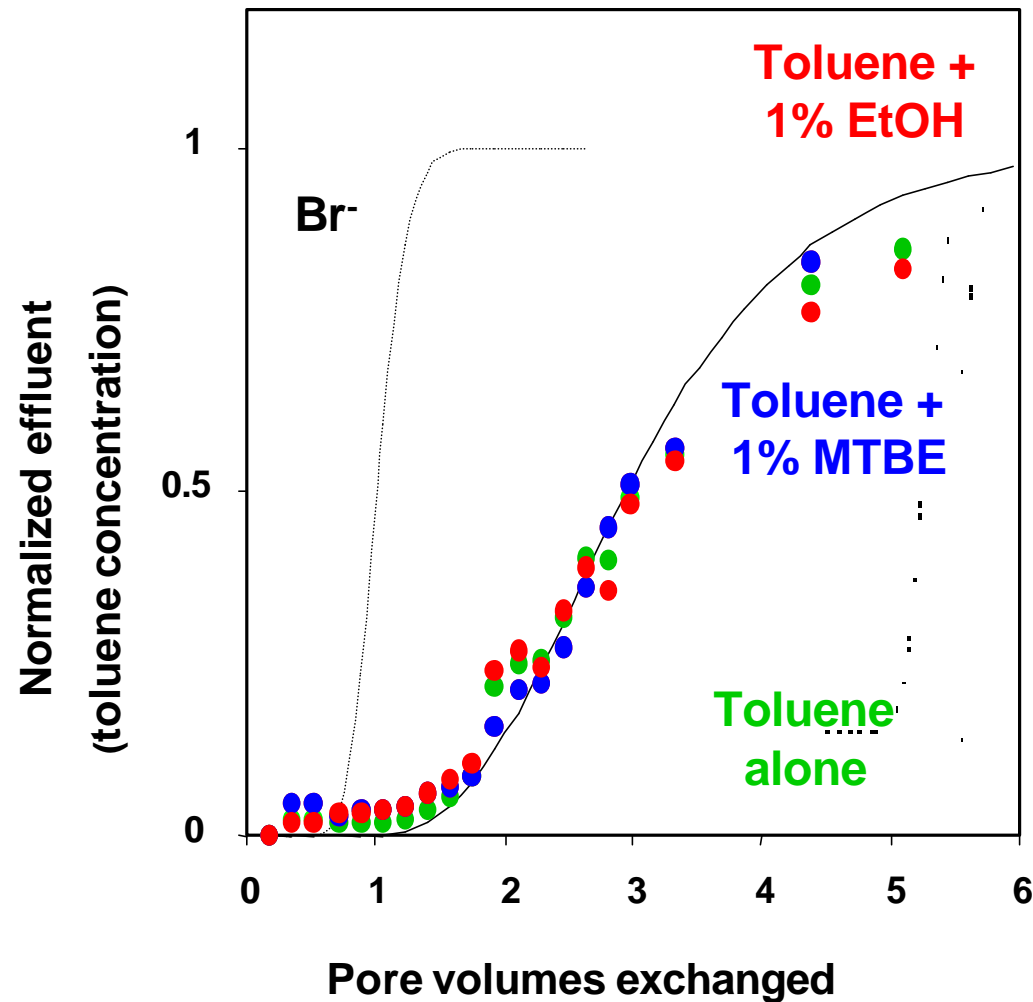


Column Profiles  
(Natural attenuation)





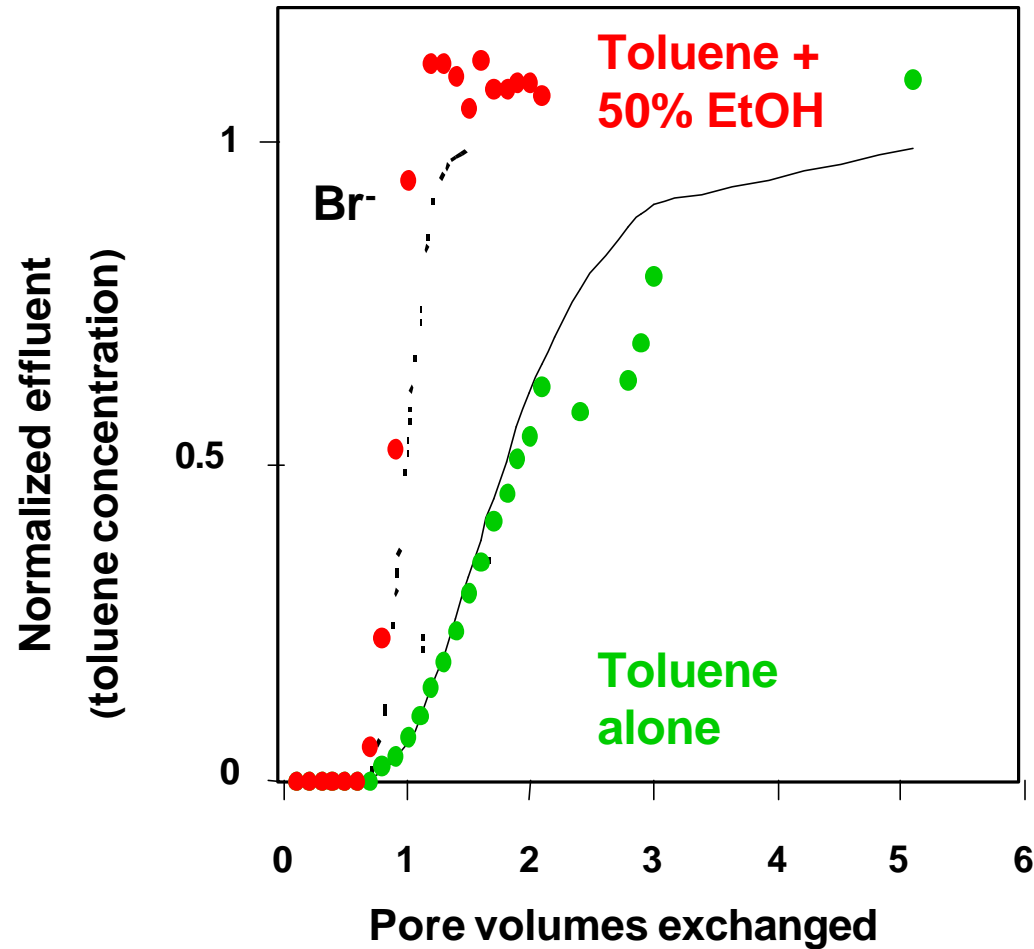
# No Effect of EtOH or MTBE on Sorption-Related BTX Retardation



$$R_f = 3.4 \text{ for all cases}$$

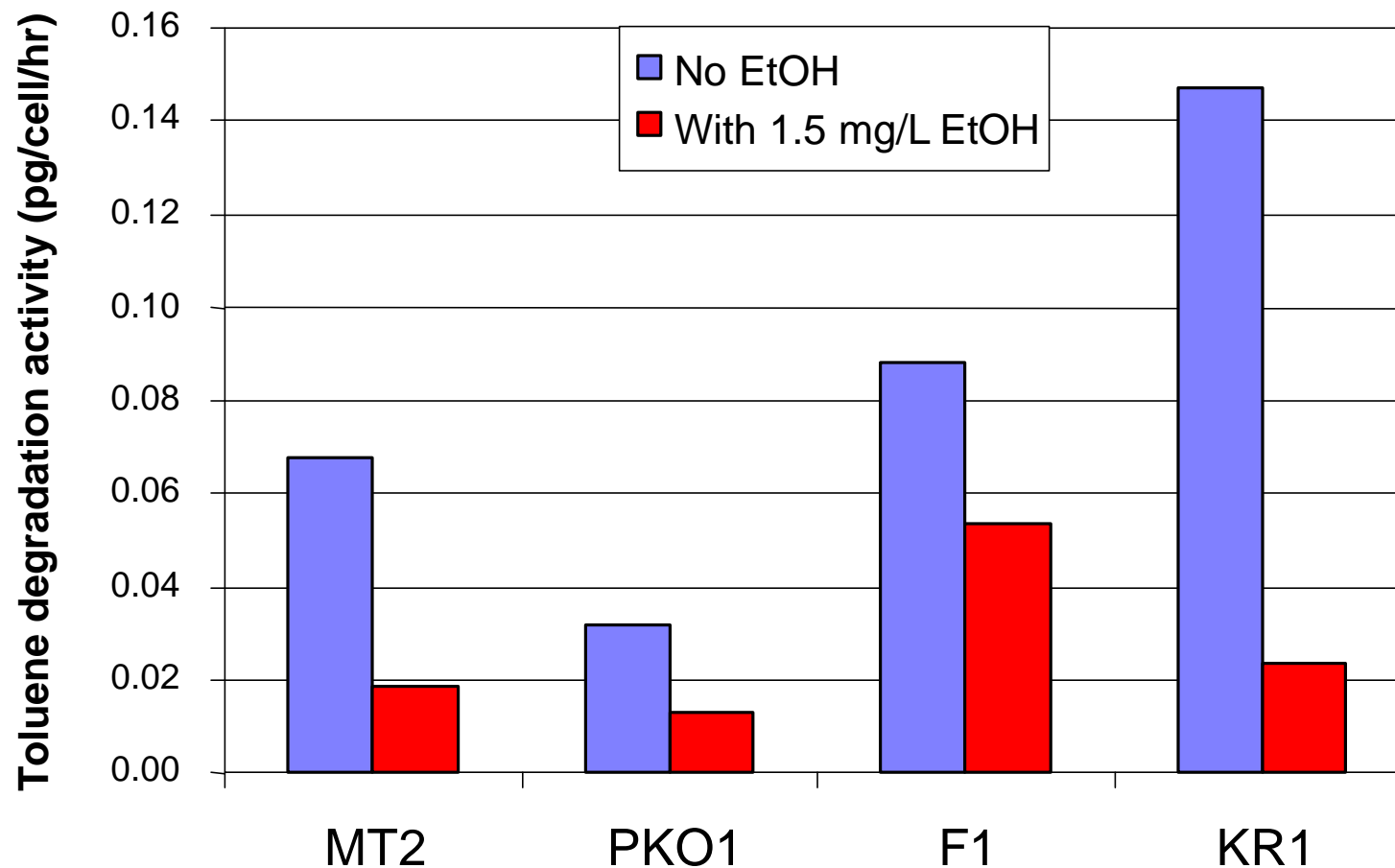


## Effect of **High EtOH Conc.** on Sorption-Related BTX Retardation



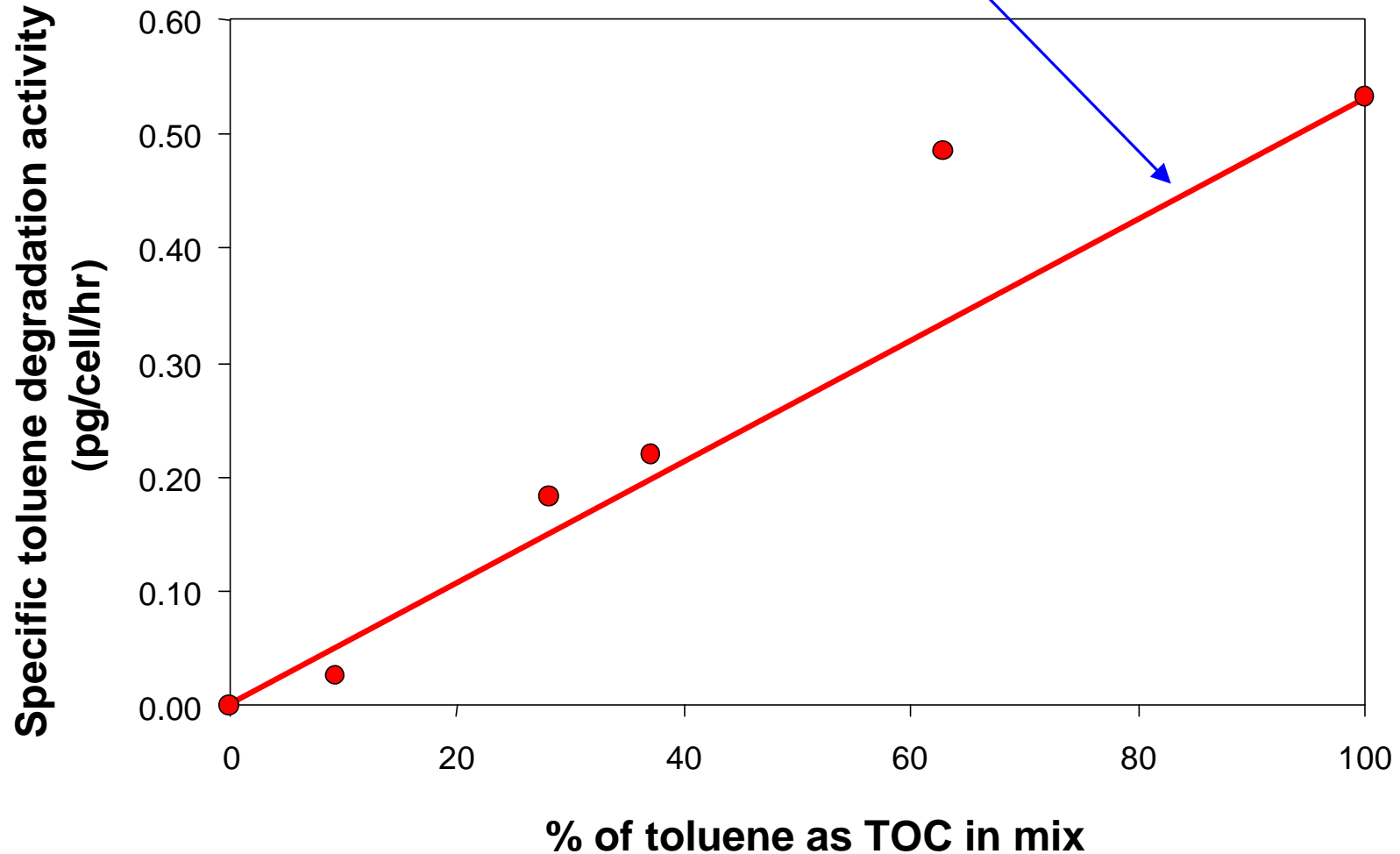
$R_f = 1$  with 50% EtOH

## Effect of ethanol on aerobic toluene degradation activity in chemostats with different archetypes, fed 1 mg/L toluene



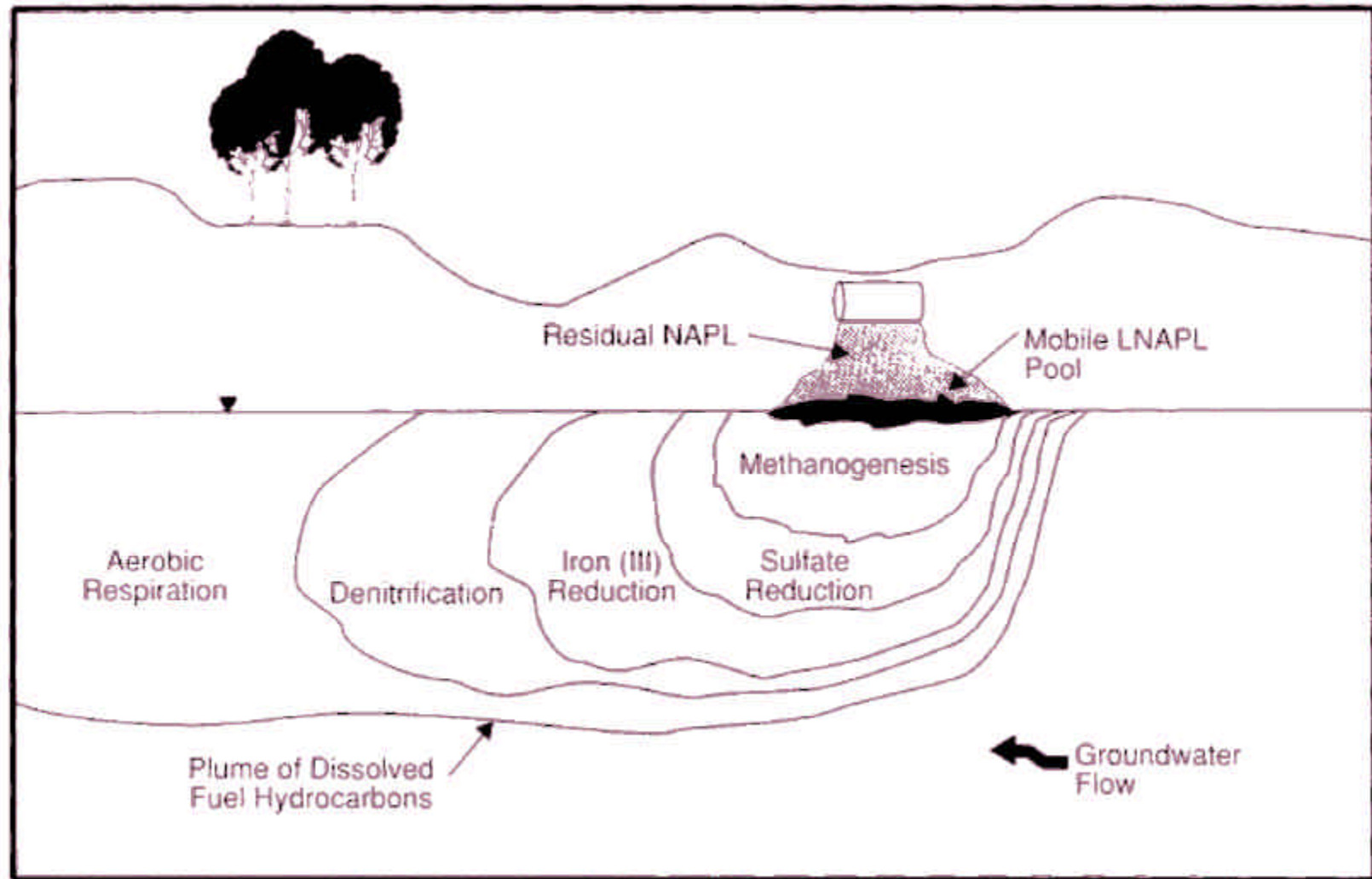
# The specific degradation rate of toluene by *P. mendocina* KR1

$\text{Rate per cell (BTX)}_{\text{mix}} = \text{Rate per cell (BTX)}_{\text{alone}}? \text{ (BTX fraction in mix, as TOC)}$



# Geochemical evolution of BTX-contaminated groundwater

(Source: Wiedemier et al., 1999)



**Days to degrade 50 % of toluene (1-2 mg/L) in microcosms with aquifer material from different sites under different electron acceptor conditions**

Site	Aerobic			Denitrifying			Iron-reducing			Sulfate-reducing			Methanogenic		
	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH
A	7		6	32		30	29		> 70	> 70		> 70	57		35
B	1	1	7	4	4	4	5	5	18	11	11	7	5	5	34
C	11		14	> 48		14	13		17	24		33	> 54		> 56
D	3	14	>13	51	36	30				30	8	11	38	16	26

Site A = Tracy site, no known previous BTEX exposure.

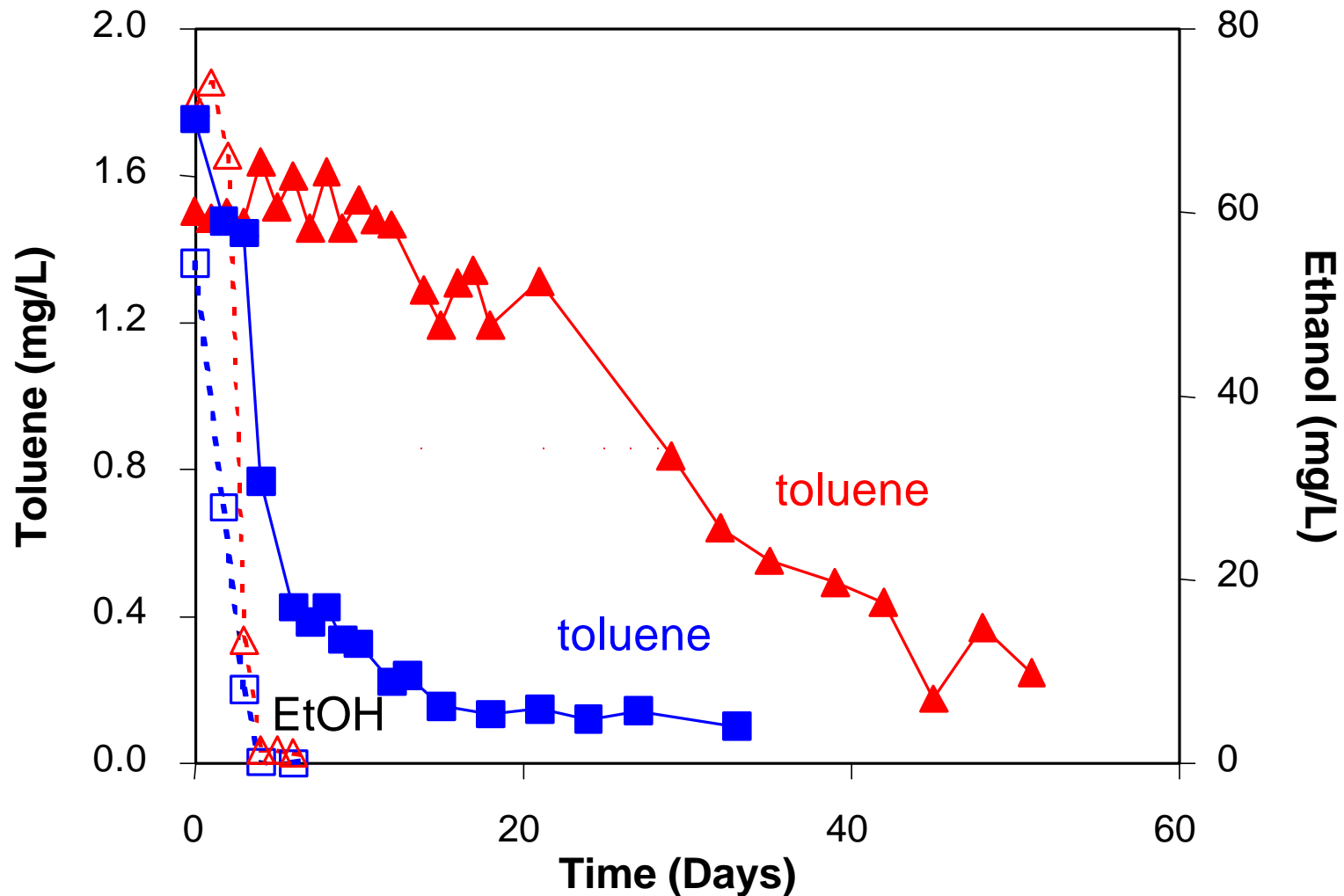
Site B = Travis AFB site, contaminated with BTEX and MTBE.

Site C = NW bulk terminal site, neat EtOH release over pre-existing BTEX contamination.

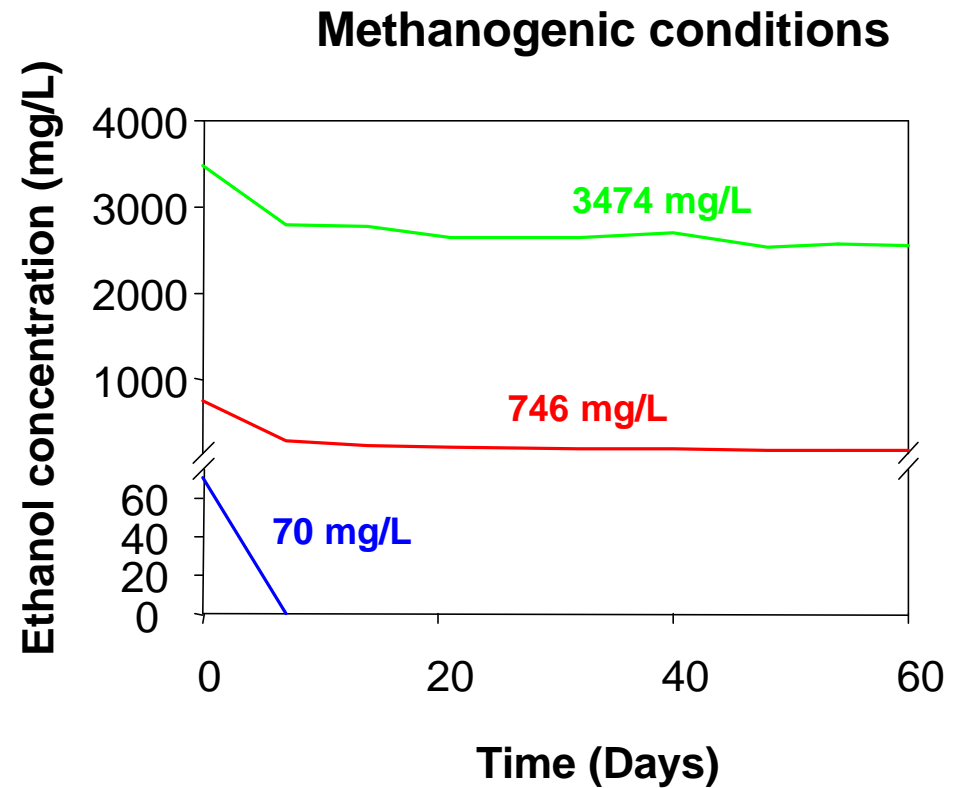
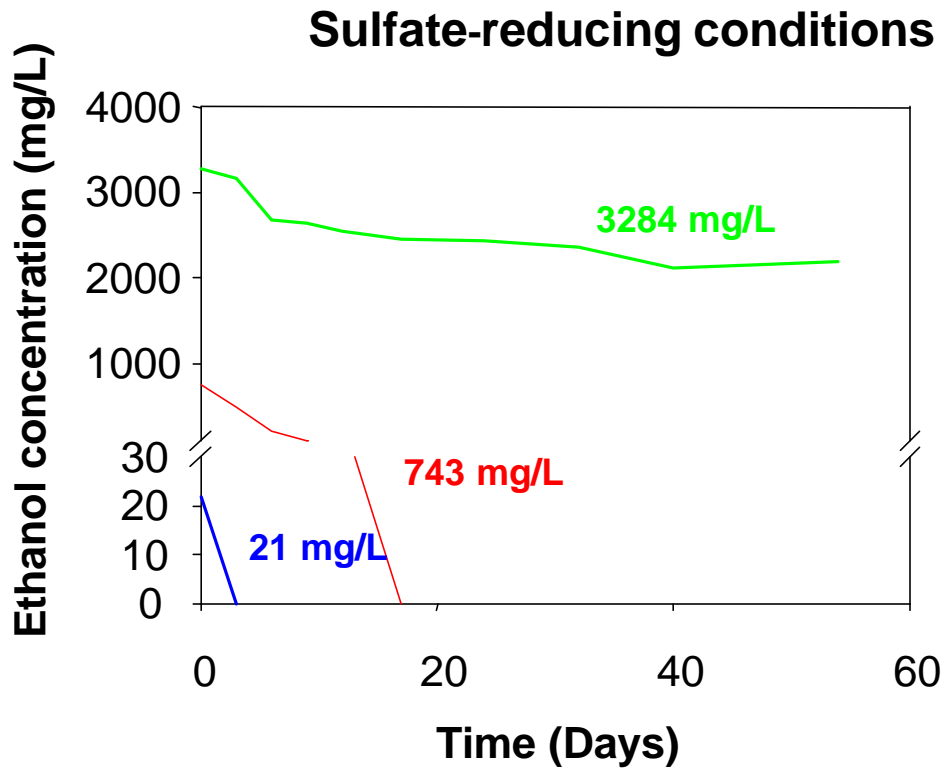
Site D = Sacramento site, contaminated with BTEX and MTBE.

EtOH or MTBE added at 100 mg/L

## Toluene and ethanol degradation in denitrifying microcosms from **contaminated** and **uncontaminated** sites

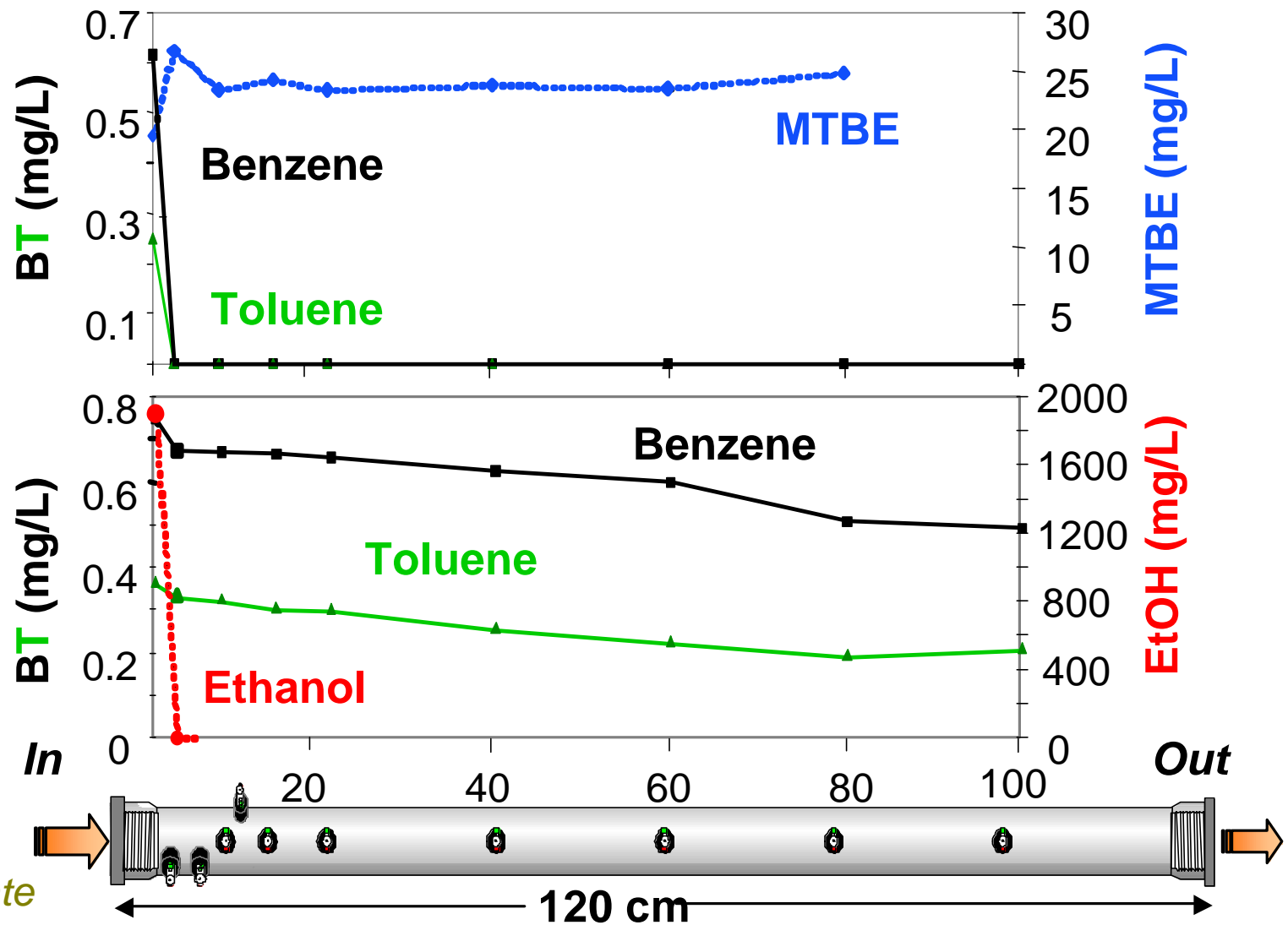


**Ethanol concentrations exceeding 3,000 mg/l  
were not degraded in anaerobic microcosms**



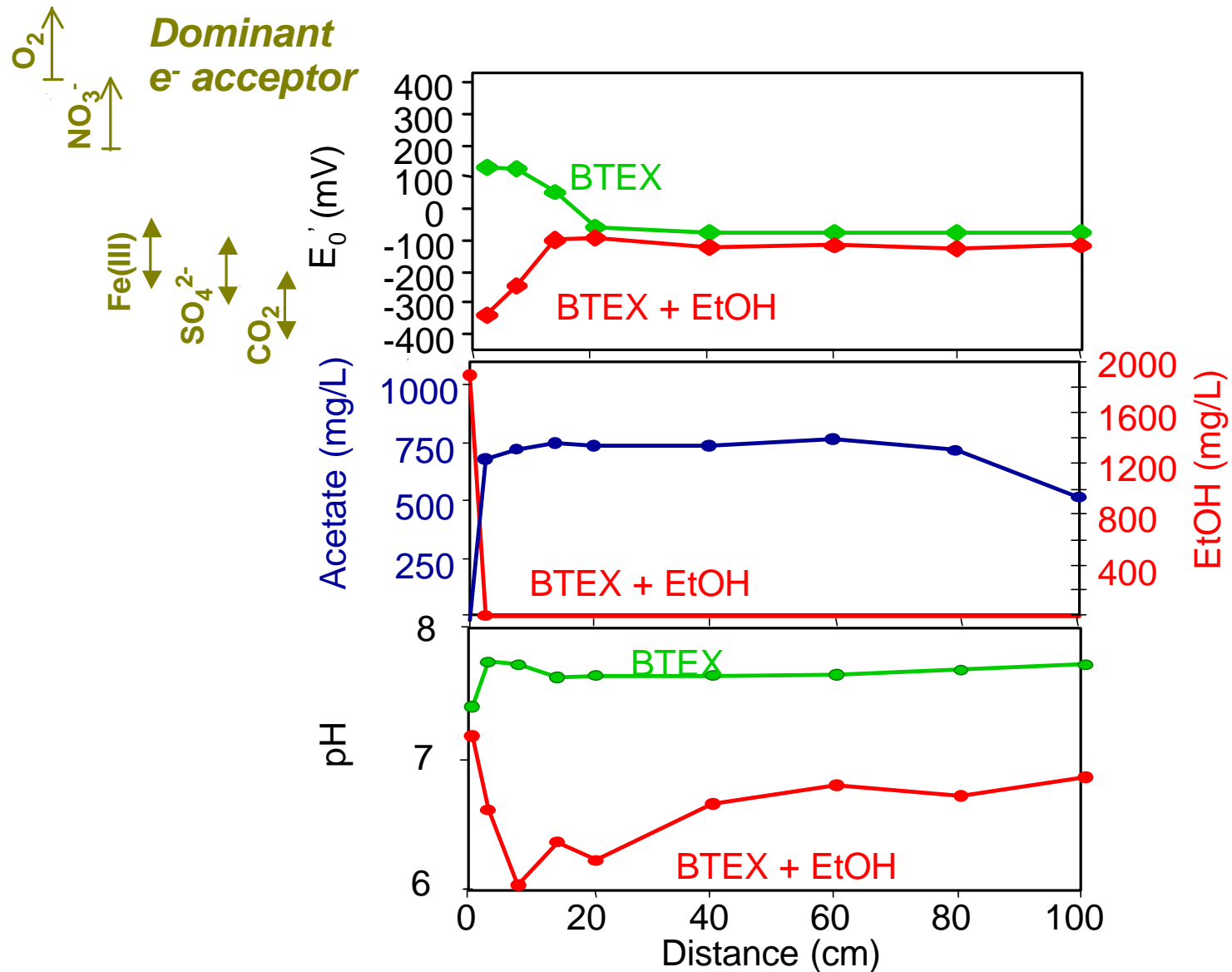


## Effect of **Ethanol** and **MTBE** on BTX Natural Attenuation



*HRT = 5.5 days  
8 ppm DO  
30 ppm nitrate  
100 ppm sulfate  
1000 ppm bicarbonate*

# Effect of ethanol on redox potential, acetate production and pH



# DGGE Analysis of the Effect of EtOH and MtBE on Microbial Community (by Microbial Insights, Inc.)

BTEX Alone		BTEX + EtOH		BTEX + MtBE	
Inlet	40cm	Inlet	40cm	Inlet	40cm
A	D	E	H	L	
B			I		
			J		
		F	K		M
C		G			

## Dominant species

**A - *Geobacter akaganeitreducens***

**B - *Geobacter sp.***

**C - *Clostridium sp.***

**D - *Azoarcus sp.***

**E - *Campylobacter sp.***

**F - *Clostridium sp.***

**G - *Desulfovibrio burkinensis***

**H - *Sporomusa sp.***

**I - Clone WCHB1-71**

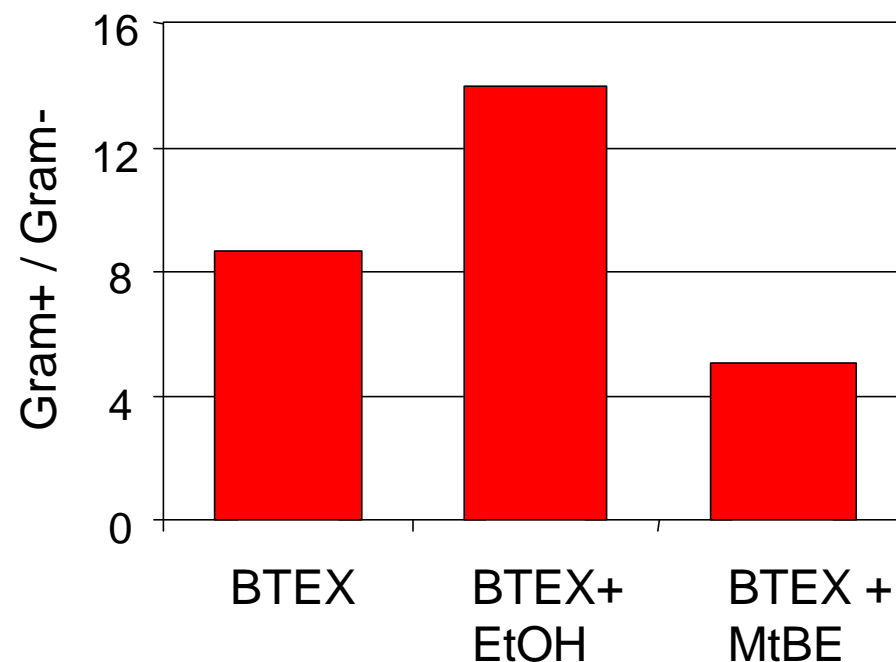
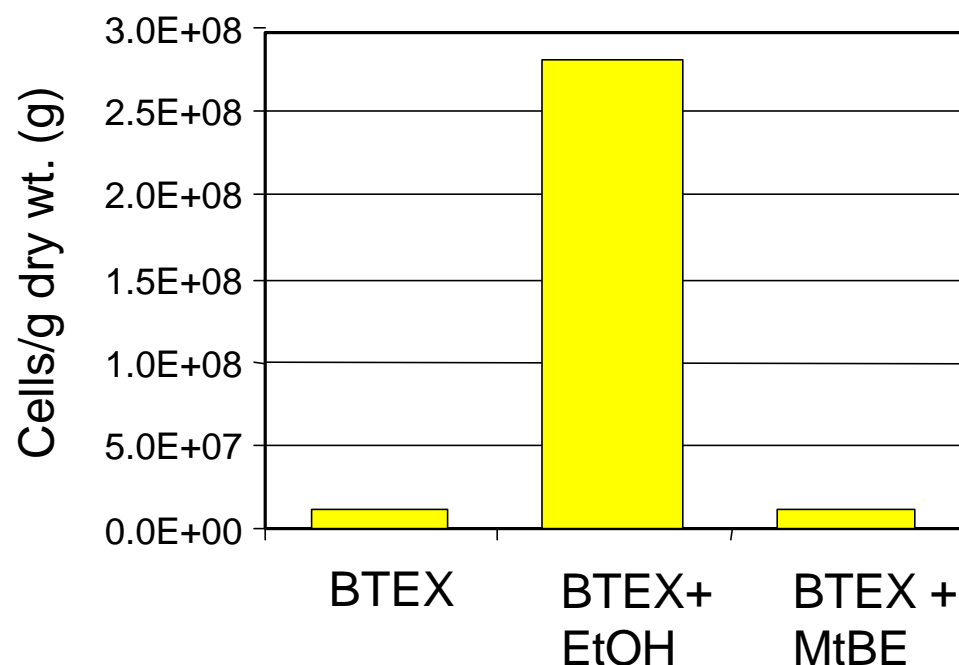
**J - Failed**

**K - Clone SJA-181**

**L - *Geobacter akaganeitreducens***

**M - *Slackia exigua***

## PLFA Analysis of Microorganisms in the Inlet of the Columns



*EtOH increased the biomass concentration (10X)  
and the relative abundance of Gram+ bacteria*

## Conclusions

- † Cosolvent effects are unlikely at gasohol-contaminated sites (i.e., [EtOH] < 10,000 mg/L) - ***but important for neat releases.***
- † Ethanol itself is not a major groundwater quality problem, but it could ***increase BTEX plume lengths*** (preferential degradation and depletion of nutrients and electron acceptors that could otherwise be used for BTEX biodegradation).
- † ***MTBE should not affect BTEX behavior***, but itself is a major concern in drinking water supplies.